

⑫

EUROPEAN PATENT APPLICATION

⑳ Application number: 83108599.8

⑤① Int. Cl.³: **C 08 F 8/30**

㉔ Date of filing: 31.08.83

㉔ Priority: 01.09.82 JP 153028/82

㉔ Applicant: SUMITOMO CHEMICAL COMPANY, LIMITED,
15 Kitahama 5-chome Higashi-ku, Osaka-shi Osaka-fu
(JP)

④③ Date of publication of application: 11.04.84
Bulletin 84/15

㉔ Inventor: Kataoka, Yushin, 7-34, Maedacho, Niihama-shi
(JP)
Inventor: Matsuda, Masaaki, 4-5, Hoshigoecho,
Niihama-shi (JP)
Inventor: Ochi, Kenji, 11-8, Maedacho, Niihama-shi (JP)
Inventor: Aoi, Masahiro, 3, Kitashinmachi, Niihama-shi
(JP)

④④ Designated Contracting States: DE FR GB NL

㉔ Representative: Vossius Vossius Tauchner Heunemann
Rauh, Siebertstrasse 4 P.O. Box 88 07 67,
D-8000 München 86 (DE)

⑤④ Chelate resins, process for their production and their use.

⑤⑦ Described are chelate resins having a functional group of
the formula: $\text{—C} = \text{NOH}$, wherein R_1 and R_2 are each



independently hydrogen, alkyl, aminoalkyl, phenyl or a substi-
tuted group thereof and another functional group of the formu-
la: $\text{—C} = \text{NH}$, wherein R_3 is amino, alkylamino,



polyethylenepolyamino, hydrazo, hydrazino, hydrazono, ami-
dino, guanidino, semicarbazide or a substituted group thereof.
These resins have an excellent adsorption capacity for metal
ions.

EP 0 105 201 A2

31 AUG 1963
0105201

Our Ref.: S 601 EP
Case: A8018-02

SUMITOMO CHEMICAL COMPANY, LIMITED
OSAKA, JAPAN

CHELATE RESINS, PROCESS FOR THEIR PRODUCTION
AND THEIR USE

This invention relates to chelate resins and a process for producing the same and their use for removing metal ions from liquids containing metal ions.

Chelate resins are very useful for the purification of industrial water, the treatment of waste water, 5 the recovery of valuable metal elements, and the like because when they are used, metal ions can selectively be removed from a liquid containing the metal ions.

It has heretofore been well known that a resin having amidoxime groups is produced by reacting a 10 resin having nitrile groups with hydroxylamine and/or a derivative thereof, and that the thus obtained resin satisfactorily adsorbs metal ions such as uranium, gold, iron, mercury, copper, lead and the like (U.S. Patent No. 3,088,799, Published Unexamined Japanese 15 Patent Application Nos. 53,593/76, and 126,088/78). However, said chelate resin has small adsorption capacity and is desired to be improved in this point.

Recently, in order to improve such a disadvantage of said chelate resin, there has been proposed a 20 process for producing a chelate resin having amidoxime groups by subjecting to polymerization a monomer mixture comprising a crosslinking agent selected from the group consisting of polyacrylates of polyalkylene polyols whose alkylene groups have 2 to 4 carbon atoms, and 25 polymethacrylates of said polyols, and an ethylenically

0105201

1 unsaturated compound having one or more nitrile groups,
and then reacting the resulting polymer with hydroxyl-
amine (Published Unexamined Japanese Patent Application
No. 53,106/81). The improved chelate resin described
5 above has an improved metal ion adsorption rate as compared
with conventional resins having amidoxime groups but does
not always have a sufficiently improved adsorption
capacity for metal ions. Therefore, when a large amount
of a liquid is subjected to adsorption treatment, the im-
10 proved chelate resin is disadvantageous, for example, in
that the amount treated per unit time decreases, that
many treating apparatuses are needed, and that the
construction and operation costs increase.

In consideration of these circumstances, in
15 order to produce an amidoxime group type chelate resin
having an excellent adsorption capacity and a high adsorp-
tion rate as compared with well-known amidoxime group
type chelate resins, the present inventors have
devoted themselves to investigations to accomplish
20 this invention.

This invention provides a chelate resin having
a functional group represented by the formula:



wherein R_1 and R_2 are each independently a hydrogen atom,

- 1 an alkyl group, an aminoalkyl group, a phenyl group or substituted group thereof, and a functional group represented by the formula:



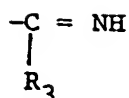
- wherein R_3 is an amino group, an alkylamino group, a polyethylenepolyamino group, a hydrazo group, a hydrazino group, a hydrazono group, an amidino group, a guanidino group, a semicarbazide group, or a substituted group thereof.

- This invention further provides a process for producing the above-mentioned chelate resin, which comprises reacting a resin having nitrile groups with hydroxylamine and/or its derivative and an amino compound other than hydroxylamine and/or its derivative (hereinafter referred to merely as "the amino compound").

- The chelate resin of this invention having in its resin substrate a functional group represented by the formula:



and a functional group represented by the formula:



(II)

1 is characterized in that it has much larger metal ion adsorption ability than the well-known chelate resins having only amidoxime groups.

As the functional group represented by the
 5 formula (II), functional groups in which R_3 is an amino group, a hydrazino group, an alkylamino group having 1 to 4 carbon atoms, or a polyethylenepolyamino group having 2 to 10 carbon atoms and 2 to 6 nitrogen atoms, are preferred. Such a combination that R_1 and R_2 are each a
 10 hydrogen atom and R_3 is a hydrazino group or a polyethylene-polyamino group having 2 to 10 carbon atoms and 2 to 6 nitrogen atoms is particularly preferred. The equivalent ratio between the functional groups represented by each of the general formulas (I) and (II), i.e., (II)/(I),
 15 is preferably 0.1 to 1. When the equivalent ratio is less than 0.1, the effect of improving the adsorption ability for metal ions is insufficient. On the other hand, even when the equivalent ratio is increased, the effect of improving the adsorption ability for metal ions does
 20 not increase proportionately thereto, and therefore the equivalent ratio is usually adjusted to 1 or less.

The chelate resin of this invention can be produced by reacting a resin having nitrile groups with hydroxylamine and/or its derivative and the amino
 25 compound.

As the resin having nitrile groups used in

1 the process of this invention, the following polymers,
copolymers and resins can be usually used:

- (1) Polymers of a vinyl cyanide series monomer or
copolymers of a vinyl cyanide series monomer and an
5 ethylenically unsaturated monomer copolymerizable there-
with. Examples of the vinyl cyanide series monomers are
acrylonitrile, α -chloroacrylonitrile, vinylidene
cyanide, methacrylonitrile, ethacrylonitrile, fumaro-
dinitrile, crotononitrile, 2-cyanoethyl acrylate, 2-
10 cyanoethyl methacrylate and the like. Examples of the
ethylenically unsaturated monomer copolymerizable therewith
are divinylbenzene, diethylene glycol dimethacrylate,
ethylene glycol dimethacrylate, polyethylene glycol
dimethacrylate, vinyl acetate or the like.
- 15 (2) Resins obtained by reacting a polymer having
an amine-reactive group (hereinafter referred to as
"the resin having an amine-reactive group") with a nitrile
compound having one or more amino or imino groups.
Examples of the amine-reactive group are a chloromethyl
20 group, a sulfonyl chloride group, a carbonyl chloride
group, an isocyanate group, an epoxy group, an aldehyde
group and the like. Examples of the resins having an
amine-reactive group are a styrene-divinylbenzene
copolymer, a phenol resin, a polyethylene, a poly-
25 propylene, a polyvinyl chloride and the like. Examples
of the nitrile compound having one or more amino groups
or imino groups are aminoacetonitrile, aminomalononitrile,
diaminomaleonitrile, dicyandiamide, iminodiacetonitrile,

1 1-amino-2-cyanoethane, 4-aminobenzonitrile, 1-amino-3-
cyanopropane and the like. But, the resin having nitrile
groups is not limited to those obtained from the above
mentioned nitrile compounds.

5 There are particularly preferably used polymers
of a vinyl cyanide series monomer such as acrylonitrile,
methacrylonitrile, ethacrylonitrile, fumarylonitrile
or vinylidene cyanide, or copolymers of any of these
vinyl cyanide series monomers and divinylbenzene,
10 diethylene glycol dimethacrylate, ethylene glycol
dimethacrylate, polyethylene glycol dimethacrylate,
vinyl acetate or the like.

The resin having nitrile groups is not
particularly limited in its polymerization degree so
15 long as it is insoluble in water, though in general,
those having a polymerization degree of about 500 or
more are preferably used.

As to the form of the resin having nitrile
groups, resins in any of powder form, fiber form,
20 honeycomb form, particle form, spherical form and
liquid form may be used, and the form may properly be
selected depending on purposes, though in general,
spherical or powdery resins are preferably used from the
viewpoint of handling.

25 As the hydroxylamine and/or the derivative
thereof reacted in order to form amidoxime groups in the
resin having nitrile groups which are used in practicing
the process of this invention, any one may be used so

1 long as it reacts with the nitrile groups to form
 amidoxime groups represented by the formula (I). As
 such hydroxylamine and/or derivatives thereof, there are
 exemplified hydroxylamine, N-methylhydroxylamine,
 5 N-ethylhydroxylamine, N-aminomethylhydroxylamine, N-
 phenylhydroxylamine, p-(hydroxylamino)phenol, o-acetyl-
 hydroxylamine, and hydrochlorides, sulfates, nitrates,
 phosphates, acetates and the like thereof.

As the amino compound used in order to impart
 10 a group of the formula (II) to the chelate resin in
 practicing the process of this invention, any one may be
 used so long as it reacts with the nitrile groups, has
 such basicity that it can react with acid ions in a
 liquid to form a salt, and forms a complex with a
 15 metal ion. As such an amino compound, there are exempli-
 fied, amines such as ammonia, methylamine, ethylamine,
 propylamine, butylamine and the like; hydrazine and its
 derivatives such as hydrazine, hydrazine hydrate, phenyl-
 hydrazine, p-hydrazinophenol, p-hydrazinobenzoic
 20 acid, p-hydrazinobenzenesulfonic acid, 1-amino-
 piperazine, N-methylhydrazine, 11-oxa-3,4,7,8,14,15-
 hexaazaheptadecane-1,17-diol, acetaldehyde hydrazone,
 hydrazinoethanol, isothiosemicarbazide, thiocarbono-
 hydrazide, semicarbazide and the like; azanes, azenes
 25 and derivatives thereof, such as triazane, triazene,
 tetrazane, tetrazene, tetrazadiene, pentazane, 1-
 methyltriazane, 1-methyl-3-propyltriazane, 3-methyl-
 triazene, 3-methyl-1-tetrazene, ethyltetrazanoacetate

- 1 and the like; amidine and its derivatives such as acetamidine, hexaneamidine, cyclohexanecarboxy-
amidine, p-amidino-1-benzoic acid and the like;
guanidine and its derivatives such as guanidine,
5 biguanide, 1,3-dimethylguanidine, 1,1,2-trimethyl-
guanidine and the like; amidoxime and its derivatives
such as formamidoxime, acetamidoxime, imidazole-2-
carboxamide-o-ethyloxime, N-methylacetamidoxime
and the like; amidrazone and its derivatives
10 such as benzamide hydrazone, benzamido hydrazido
imide, hydrazine, 2-thenohydrazide hydrazone,
N²,N⁴-dimethyl-4-thiazolecarbohydrazide hydrazone,
benzaldehyde hydrazone and the like; formazan and its
derivatives such as formazan, 3-phenyl formazan,
15 1,3-diphenylformazan, 1,3-dimethylformazan and the
like; and polyethylenepolyamines and their derivatives
such as ethylenediamine, diethylenetriamine, triethylene-
tetramine, tetraethylenepentamine, pentaethylenhexamine,
hexamethylenediamine, trimethylenediamine, tetramethylene-
20 diamine, pentaethylenediamine and the like.

The reaction of the resin having nitrile groups with the hydroxylamine and/or its derivative and the amino compound is usually effected by a method wherein the resin having nitrile groups is reacted with hydroxyl-
25 amine and/or its derivative and the amino compound which coexist with each other, to form functional groups of each of the formulas (I) and (II) at the same time. Said reaction can also be effected by a method comprising

- 1 previously reacting the resin having nitrile groups with
hydroxylamine or its derivative, then adding the amino com-
pound, and further allowing the resulting mixture to reac-
tion, or by a method comprising previously reacting the
5 resin having nitrile groups with the amino compound, and
then reacting the reaction product with hydroxylamine
and/or its derivative.

- The reaction of the resin having nitrile groups
with hydroxylamine and/or its derivative and the amino
10 compound can be effected at ordinary temperatures (about
20°C) to 150°C, preferably at 50° to 120°C in the
absence of a solvent or in the presence of a solvent.
Examples of the solvent are water, methanol, ethanol,
propanol, butanol, N,N-dimethylformamide, formamide,
15 N,N-dimethyl sulfoxide, toluene, xylene, carbon
tetrachloride, 1,2-dichloroethane and the like. When
the reaction temperature is lower than ordinary tempera-
tures, the reaction rate decreases, so that the reaction
must be effected for a long time, and when the reaction
20 temperature is higher than about 150°C, a phenomenon
of the decomposition of the formed functional groups
occurs. Therefore, such reaction temperatures are not
preferable.

- The reaction is effected at the temperature
25 described above, usually for about 0.1 to 24 hours,
preferably for 0.5 to 6 hours. But a still longer
reaction time may be used. Although the reaction is usual-
ly effected at atmospheric pressure, it may be effected

1 under pressure.

As to the reaction proportions of the hydroxyl-
amine and/or the derivative thereof and of the amino
compound to the resin having nitrile groups, it is
5 sufficient that the hydroxylamine and/or the derivative
thereof and the amino compound are used in amounts of
1/5 mole or more and 1/20 mole or more, respectively, per
equivalent of the nitrile groups in the resin. However,
since the employment of the reactants in larger amounts
10 than are necessary is accompanied by recovery treatment
after the reaction and hence makes the treatment
procedure troublesome, the hydroxylamine and/or the
derivative thereof and the amino compound are preferably
used in amounts in the ranges from 2/5 to 10 moles and
15 from 1/10 to 3 moles, respectively, per equivalent of
the nitrile groups in the resin. When the reaction pro-
portions of the hydroxylamine and/or the derivative thereof
and of the amino compound to the resin having nitrile
groups are smaller than those described above, the amounts
20 of chelate-forming functional groups introduced decreases,
so that the metal adsorption capacity of the resulting
reaction product chelate resin decreases. Therefore,
it is not desirable.

When the hydroxylamine and/or the derivative
25 thereof used in the above-mentioned reaction is a salt
with hydrochloric acid, sulfuric acid, nitric acid,
phosphoric acid, acetic acid or the like, it is
sufficient that the resin having nitrile groups is

1 reacted with the hydroxylamine derivative and the amino
compound in the presence, in the reaction system, of the
same amount as said salt or more of sodium hydroxide,
potassium hydroxide, a tertiary amine such as trimethyl-
5 amine, triethylamine, pyridine, N,N-dimethylaniline or
the like, or the aforesaid amino compound.

The reaction product produced in the manner
described above may be used as a chelate resin as it is
or after being washed and then dried.

10 The chelate resin produced by the process of
this invention contains groups of each of the formula (I)
and the formula (II) as main functional groups, and
although the reason why the chelate resin produced by the
process of this invention has a higher adsorption rate
15 and a larger adsorption capacity than those of the
heretofore well-known amidoxime type chelate resins
is not apparent, it is presumed to be as follows.

That is to say, the reason is thought to
be that in the reaction of the resin having nitrile
20 groups with the hydroxylamine and/or the derivative
thereof and the amino compound, owing to the electrical
interaction between the amino compound and the nitrile
groups in the resin, the reactivity of the hydroxylamine
and/or the derivative thereof with the nitrile groups
25 is improved as compound with that in a system free from
the amino compound, resulting in an increase of the amount
introduced of the functional group represented by the
formula (I), and that owing to the interaction between

0105201

- 1 the functional group represented by the formula (II),
which is formed by the reaction of the nitrile groups with
the amino compound, and the functional group represented
by the formula (I), the chelate adsorption ability
5 is increased as compared with that in the case where the
functional group of the formula (I) alone is present.

The chelate resin produced by the process of
this invention can very effectively be utilized for the
adsorption and removal of metal ions such as uranium,
10 gallium, indium, copper, iron, mercury, lead and the
like.

According to the process of this invention
described above in detail, there is such an advantage in
that there can be produced a chelate resin having a
15 high adsorption rate and large adsorption capacity
as compared with the well-known amidoxime type chelate
resins. Accordingly, when the chelate resin obtained by
the process of this invention is used, the superficial
velocity in column can be increased owing to the high
20 adsorption rate and the large adsorption capacity:
therefore said chelate resin is very effective for
treating a large amount of a liquid, has advantages of,
for example, low construction and operation costs of the
treating facilities, and hence has a very high industrial
25 value.

This invention is further explained below in
more detail referring to Examples, wherein all parts and
percents are by weight unless otherwise specified.

1 Example 1

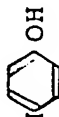
To 61 parts of a resin having nitrile groups,
i.e. an acrylonitrile-divinylbenzene copolymer
having a degree of crosslinking of 10 mole% and a
5 particle size of 20 to 50 mesh were added 139 parts
of hydroxylamine hydrochloride, 100 parts of hydrazine
hydrate and 300 parts of water. The resulting mixture
was reacted at 90° to 107°C for 4 hours, followed by
filtration and washing, to obtain 169 parts by weight
10 (undried) of a chelate resin. In the chelate resin
obtained, there were detected a functional group

$$\begin{array}{c} \text{-C} = \text{NOH} \\ | \\ \text{NH}_2 \end{array}$$
in an amount of 6.0 mole/liter resin and
a functional group
$$\begin{array}{c} \text{-C} = \text{NH} \\ | \\ \text{NHNH}_2 \end{array}$$
in an amount of 1.8 mole/liter
resin. To 50 ml of an aqueous sodium aluminate solution
15 containing 197 ppm of Ga obtained from the production
process of alumina by the Bayer process was added 7 ml of
the chelate resin obtained, and the resulting mixture
was shaken for 20 hours and then separated into the
chelate resin and an aqueous layer. The concentration
20 of Ga remaining in the aqueous layer was measured to be
14 ppm. To 50 ml of enriched sea water containing
110 ppm of U was added 1 ml of the chelate resin
obtained, and the resulting mixture was shaken for 20
hours and then separated into the chelate resin and an
25 aqueous layer. The concentration of U remaining in the
aqueous layer was measured to be 17 ppm.

1 Examples 2 to 13


A reaction was effected in the same manner as in Example 1, except that the hydrazine hydrate, i.e., the amino compound used in Example 1 and the used amount thereof were replaced by the individual amino compounds and amounts shown in Table 1, to synthesize a chelate resin. The thus obtained chelate resins were subjected to performance characteristic tests. The results are shown in Table 1.

Table 1

Exam- ple	Amino. compound.		Chelate resin			Adsorption ability test	
	Kind	Amount	Yield (dried)	Functional group (I) mole/liter resin	Functional group (II) mole/liter resin	Ga (ppm)	U (ppm)
2	p-Hydrazino- phenol	parts 186	parts 153	-C=NOH NH_2	-C=NH NHNH 	27	21
3	2-Hydrazino- ethanol	114	167	"	-C=NH $\text{NHNHCH}_2\text{CH}_2\text{OH}$	19	21
4	Guanidine	89	154	"	-C=NH HNC (=NH) -NH_2	12	14
5	1,1,2-Tri- methylguanidine	152	183	"	-C=NH $\text{HN-C (=N-CH}_3\text{)N(CH}_3\text{)}_2$	13	14

- Cont'd -

Table 1 (cont'd)

6	Formamidoxime	90	147	$\begin{array}{c} \text{-C=NOH} \\ \\ \text{NH}_2 \end{array}$	4.9	$\begin{array}{c} \text{-C=NH} \\ \\ \text{HNCH=NOH} \end{array}$	1.5	23	20
7	Formhydrazide	81	147	"	4.9	$\begin{array}{c} \text{-C=NH} \\ \\ \text{HNNHCOH} \end{array}$	1.5	24	21
8	Formamidine	66	153	"	5.0	$\begin{array}{c} \text{-C=NH} \\ \\ \text{HNCH=NH} \end{array}$	1.5	21	19
9	Benzaldehyde hydrazone	180	143	"	4.7	$\begin{array}{c} \text{-C=NH} \\ \\ \text{HNN=NCH-} \end{array}$ 	1.2	28	23
10	Ethylenediamine	90	156	"	5.8	$\begin{array}{c} \text{-C=NH} \\ \\ \text{HNCH}_2\text{CH}_2\text{NH}_2 \end{array}$	1.7	15	15
11	Diethylenetri- amine	155	184	"	5.9	$\begin{array}{c} \text{-C=NH} \\ \\ \text{HN(CH}_2\text{CH}_2\text{NH)}_2 \end{array}$	1.7	13	14

- Cont'd -

0105201

Table 1 (Cont'd)

12	Triethylene- tetramine	219	189	$\begin{array}{c} \text{-C=NOH} \\ \\ \text{NH}_2 \end{array}$	5.9	$\begin{array}{c} \text{-C=NH} \\ \\ \text{HN(CH}_2\text{CH}_2\text{NH)}_3\text{H} \end{array}$	1.6	13	14
13	Semicarbazide	144	153	"	4.8	$\begin{array}{c} \text{-C=NH} \\ \\ \text{HNNHCONH}_2 \end{array}$	1.4	25	22

0105201

1 Example 14

To 82 parts of a resin having nitrile groups, i.e., vinylidene cyanide-divinylbenzene having a degree of crosslinking of 8 mole% and a particle size of 20 to 50 mesh were added 164 parts of hydroxylamine sulfate, 267 parts of a 30% aqueous sodium hydroxide solution and 103 parts of diethylentriamine. The resulting mixture was reacted at 90° to 103°C for 2 hours, followed by filtration and washing, to obtain 284 parts (undried) of a chelate resin. In the chelate resin obtained, there were detected a functional group $\begin{array}{c} -C = NOH \\ | \\ NHNH_2 \end{array}$ in an amount of 9.8 mole/liter resin, and a functional group $\begin{array}{c} -C = NH \\ | \\ NH(CH_2CH_2NH)_2H \end{array}$ in an amount of 3.0 mole/liter resin. Performance characteristic tests on the resin obtained were carried out by the same methods as in Example 1 to find that the Ga concentration in the aqueous layer was 3 ppm and the U concentration therein 5 ppm.

Examples 15 to 18

20 A reaction was effected in the same manner as in Example 14, except that the kind and amount of the resin having nitrile groups were replaced by the individual resins and amounts shown in Table 2, to synthesize a chelate resin. The thus obtained chelate resins were subjected to performance characteristic tests. The results are shown in Table 2.

0105201

Table 2

Exam- ple	Resin having nitrile		Chelate resin				Adsorption ability test	
	Kind	Amount	Yield (un- dried)	Functional group (I) mole/liter resin	Functional group (II) mole/liter resin		Ga (ppm)	U (ppm)
15	Methacrylonitrile- divinylbenzene copolymer having a degree of cross- linking of 6 mole% and a particle size of 20 to 50 mesh	75 parts	220 parts	-C=NOH NH ₂	-C=NH HN(CH ₂ CH ₂ NH) ₂ H	2.1	11	12
16	Acrylonitrile- diethylene glycol dimethacrylate copolymer having a degree of crosslinking of 20 mole% and a particle size of 20 to 50 mesh	86	243	"	"	1.8	16	17

- Cont'd -

0105201

Table 2 (Cont'd)

17	Acrylonitrile-ethylene glycol dimethacrylate copolymer having a degree of crosslinking of 25 mole% and a particle size of 20 to 50 mesh	83	237	$\begin{array}{c} \text{-C=NOH} \\ \\ \text{NH}_2 \end{array}$	4.8	$\begin{array}{c} \text{-C=NH} \\ \\ \text{HN(CH}_2\text{CH}_2\text{NH)}_2\text{H} \end{array}$	1.7	22	23
18	Polyacrylonitrile fiber	53	147	"	6.4	"	2.2	10	12

1 Example 19

To 67 parts of a resin having nitrile groups,
i.e., an acrylonitrile-divinylbenzene copolymer having a
degree of crosslinking of 10 mole% and a particle
5 size of 20 to 50 mesh were added 94 parts of N-methyl-
hydroxylamine, 50 parts of hydrazine hydrate and 400 parts
of water. The resulting mixture was reacted at 70 to
103°C for 6 hours, followed by filtration and washing
to obtain 224 parts (undried) of a chelate resin. In the
10 chelate resin obtained, there were detected a functional
group $\text{-C} = \text{NOH}$ in an amount of 5.3 mole/liter resin, and

$$\begin{array}{c} | \\ \text{HNCH}_3 \end{array}$$
a functional group $\text{-C} = \text{NH}$ in an amount of 2.3 mole/liter

$$\begin{array}{c} | \\ \text{HNNH}_2 \end{array}$$
resin. Performance characteristic tests on the resin
obtained were carried out by the same methods as in
15 Example 1 to find that the Ga concentration in the
aqueous layer was 18 ppm and the U concentration therein
23 ppm.

Examples 20 to 23

A reaction was effected in the same manner as
20 in Example 19, except that the kinds and amounts of the
hydroxylamine derivative and the amino compound used in
Example 19 were changed as shown in Table 3, to synthesize
a chelate resin. The thus obtained chelate resins were
subjected to performance characteristic tests. The results
25 are shown in Table 3.

Table 3

Exam- ple	Hydroxylamine derivative		Amino compound		Chelate resin			Adsorption ability test	
	Kind	Amount	Kind	Amount	Yield (dried)	Functional group (I) mole/ liter resin	Functional group (II) mole/ liter resin	Ga (ppm)	U (ppm)
20	N-Ethyl- hydroxyl- amine	183 parts	Hydrazine	32 parts	270 parts	-C=NOH HNC ₂ H ₅	-C=NH NHNH ₂	21	26
21	Hydroxyl- amine hydro- chloride	69	Acetamidine	116	207	-C=NOH NH ₂	-C=NH HN-C(=NH)CH ₃	16	19
22	N-amino- methyl- hydroxylamine	126	Semi- carbazine	75	243	-C=NOH HNCH ₂ NH ₂	-C=NH HNNHCONH ₂	18	21
23	Hydroxyl- amine	99	1-Amino- piperazine	87	222	-C=NOH NH ₂	-C=NH HN-N ₂ NH	18	23

0105201

1 Comparative Example 1

A reaction was effected in the same manner as in Example 1, except that the hydrazine hydrate used in Example 1 was replaced by 80 parts of sodium hydroxide, to synthesize a chelate resin. As a result, 147 parts (undried) of the chelate resin was obtained. In the chelate resin obtained, there was detected a functional group $\text{-C} = \text{NOH}$ in an amount of 2.2 mole/liter resin.



Performance characteristic tests on the chelate resin obtained were carried out by the same methods as in Example 1 to find that the concentration of Ga remaining in the aqueous layer was 89 ppm and the U concentration 34 ppm.

Comparative Example 2

15 A reaction was effected in the same manner as in Example 14, except that 86 parts of an acrylonitrile-diethylene glycol dimethacrylate polymer having a degree of crosslinking of 20 mole% and a particle size of 20 to 50 mesh was used as a resin having nitrile groups and that 103 parts of the diethylenetriamine was omitted, to synthesize a chelate resin. As a result, 211 parts (undried) of the chelate resin was obtained. The chelate resin obtained contained a functional group $\text{-C} = \text{NOH}$



in an amount of 1.9 mole/liter resin. Performance characteristic tests on the chelate resin obtained

1 were carried out by the same methods as in Example 1
to find that the concentration of Ga remaining in the
aqueous layer was 93 ppm and the U concentration 32 ppm.

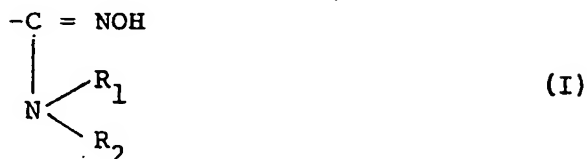
Comparative Example 3

5 Adsorption capacity tests on Duolite CS-346
(manufactured by Diamond Shamrock Corp.), a commercially
available chelate resin having amidoxime groups were
carried out by the same methods as in Example 1 to find
that the concentration of Ga remaining in the aqueous
10 layer was 114 ppm and the U concentration 37 ppm.

From Examples 1 to 23 and Comparative Examples
1 to 3, it is clear that the chelate resins obtained by
effecting the reaction of a resin having nitrile groups
with hydroxylamine and/or its derivative according to the
15 process of this invention in the presence of an amino
compound have a higher adsorption rate and a larger
adsorption capacity for metal ions than those of amidoxime
group type chelate resins produced by a well-known
process. Thus, the present invention is industrially very
20 useful.

WHAT IS CLAIMED IS:

1. A chelate resin having a functional group represented by the formula:



wherein R_1 and R_2 are each independently a hydrogen atom, an alkyl group, an aminoalkyl group, a phenyl group or a substituted group thereof and a functional group represented by the formula:



wherein R_3 is an amino group, an alkylamino group, a polyethylenepolyamino group, a hydrazo group, a hydrazino group, a hydrazono group, an amidino group, a guanidino group, a semicarbazide group or a substituted group thereof.

2. A chelate resin according to Claim 1, wherein in the functional group represented by the formula (II), R_3 is an amino group, a hydrazino group, an alkylamino group having 1 to 4 carbon atoms, or a polyethylenepolyamino group having 2 to 10 carbon atoms and 2 to 6 nitrogen atoms.

3. A chelate resin according to Claim 1, wherein in the functional group represented by the formula (I), R_1 and R_2 are independently a hydrogen atom, and in the functional group represented by the formula (II), R_3 is

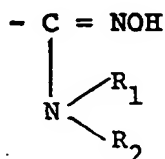
a hydrazino group or a polyethylenepolyamino group having 2 to 10 carbon atoms and 2 to 6 nitrogen atoms.

4. A chelate resin according to Claim 1, wherein the equivalent ratio of the functional group of the formula (II) to that of (I), (II)/(I), is 0.1 to 1.

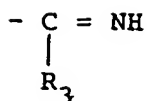
5. A process for producing a chelate resin of Claim 1, which comprises reacting a resin having nitrile groups with hydroxylamine and/or a derivative thereof and an amino compound other than the hydroxylamine and derivatives thereof.

6. A process according to Claim 5, wherein the proportions of the hydroxylamine and/or the derivative thereof and the amino compound to the resin having nitrile groups used are 1/5 mole or more of hydroxylamine and/or the derivative thereof and 1/20 mole or more of the amino compound per equivalent of the nitrile groups.

7. A chelate resin having a functional group of the formula:



wherein R_1 and R_2 are each independently a hydrogen atom, an alkyl group, an aminoalkyl group, a phenyl group or a substituted group thereof and a functional group of the formula:



wherein R_3 is an amino group, an alkylamino group, a polyethylenepolyamino group, a hydrazo group, a hydrazino group, a hydrazono group, an amidino group, a guanidino group, a semicarbazide group or a substituted group thereof, obtainable by reacting a resin having nitrile groups with hydroxylamine and/or a derivative thereof and an amino compound other than the hydroxylamine and derivatives thereof.

8. A chelate resin according to Claim 7, wherein the resin having nitrile groups is at least one member selected from the group consisting of homopolymers of acrylonitrile, methacrylonitrile, ethacrylonitrile, fumarylonitrile, and vinylidene cyanide and copolymers of a monomer selected from the group consisting of acrylonitrile, methacrylonitrile, ethacrylonitrile, fumarylonitrile and vinylidene cyanide, and a monomer selected from the group consisting of divinylbenzene, diethylene glycol dimethacrylate, ethylene glycol dimethacrylate, polyethylene glycol dimethacrylate and vinyl acetate.

9. A chelate resin according to Claim 7, wherein the resin having nitrile groups has a degree of polymerization of 500 or more.

10. A process according to Claim 5, wherein the reaction is carried out at a temperature of 20 to 150°C.

11. The use of the resins according to any one of claims 1 to 10 for removing metal ions from liquids containing metal ions.